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<b>(54) Title:</b> CYCLIC OLEFIN POLYMERIC MOISTURE BARRIERS FOR POLARIZER APPLICATIONS		
<b>(57) Abstract</b>  This invention provides novel moisture barrier protective layers for polarizers, as well as laminates comprising those layers useful for display device applications. The protective layer comprises polymers of a cyclic olefin, and the polarizing layer comprises a liquid crystalline polyester and a dichroic absorber. An illustrative laminate comprises a polarizing layer, and a protective layer, bonded by means of an intermediary adhesive layer. The protective layer offers excellent moisture protection to the laminate. The invention further provides a process to prepare such laminates.		

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## **Cyclic Olefin Polymeric Moisture Barriers for Polarizer Applications**

### **Field of the Invention**

This invention relates to cyclic olefin polymeric moisture barriers for  
5 polarizer laminates. Such cyclic olefin polymeric films provide excellent moisture  
barrier and mechanical support to the polarizing layer in the laminates, which are  
useful in applications such as, for example, liquid crystal display devices  
("LCDs").

### **Background of the Invention**

10 Polarizers are important components of liquid crystal displays. LCDs are  
widely used components in applications such as, for example, Notebook  
Personal Computers ("PCs"), calculators, watches, liquid crystal color TVs, word  
processors, automotive instrument panels, anti-glare glasses and the like. A  
useful review article, for example, is "Digital Displays" by in *Kirk-Othmer*  
15 *Encyclopedia of Chemical Technology*, Third edition, Volume 7, page 726  
(1979), Wiley-Interscience Publication, John Wiley & Sons, New York.

Typically, polarizers are used in the form of film. Traditional polarizing  
films comprise a stretched polymer film such as, for example, polyvinyl alcohol  
("PVA"), a dichroic absorber and other optional layers. The dichroic absorber is  
20 usually iodine or a dichroic dye that is absorbed in the polymer film. To provide  
physical protection during LCD manufacturing and use, the polarizer film is  
generally laminated. Lamination also prevents relaxation of dichroism, and  
provides a barrier to moisture. This moisture barrier function is particularly  
important in polarizers wherein the polarizing layer is comprised of PVA.  
25 Additionally, the type of materials used for the lamination as well as the process

of preparing the laminate are generally critical in the performance of the LCD. In one common construction of the laminate, for example, both sides of the polarizer film are laminated, thus giving rise to five individual layers: the polarizer film in the middle, flanked on either side by an adhesive layer which binds the polarizer film to a protective layer, such as, for example, polyethylene terephthalate ("PET"), polymethyl methacrylate ("PMMA"), triacetyl cellulose ("CTA"), and the like. This may further be coated with an adhesive layer, other supporting layers, and the like. The protective layer may also be bonded, via an adhesive, to a substrate.

Most commercial polarizer laminates currently use solvent cast cellulose triacetate film to provide moisture barrier to the polarizing film. However, such solvent cast moisture barriers have several disadvantages, particularly with use of environmentally noxious solvents such as for example, methylene chloride, which is commonly used in the casting of cellulose triacetate. Melt extrusion processes for film fabrication are considered preferable over solution processes since they are cheaper and avoid the use of such solvents. However, melt processing typically leads to orientation of the polymer chains in the film, thereby resulting in high birefringence, which makes the film unacceptable for many intended applications. Therefore, there is a desire in the LCD industry for improved materials for moisture barrier protective applications, as well as for improved processes.

It is, therefore, an object of this invention to provide improved protective layers for polarizer laminates.

It is an additional object of this invention to provide protective layers which exhibit low birefringence in addition to good moisture barrier properties.

It is a further object of this invention to provide laminates containing protective layers for polarizers wherein the laminates are assembled by simple processes.

It is yet another object of this invention to provide laminates comprising a  
5 polarizer layer and improved protective layers.

Other objects and advantages of the present invention will be apparent from the accompanying description and examples.

#### Summary of the Invention

10 One or more of the foregoing objects are achieved by the provision of moisture barrier protective layers for polarizers, which protective layers comprise cyclic olefin polymeric films, and by the provision of laminates comprising such protective layers and polarizing films. The cyclic olefin polymer, useful for the protective layer, may be a cyclic olefin homopolymer or a cyclic olefin copolymer  
15 ("COC"). Examples of suitable cyclic olefin monomer for the homopolymer or copolymer include, but are not limited to, norbornene, tetracyclododecene, and the like. If it is a copolymer, the comonomer is preferably an acyclic olefin. Examples of suitable acyclic olefins include, but are not limited to, ethylene, propylene, 1-butene and the like, and combinations thereof. Such cyclic olefin  
20 polymer films exhibit low birefringence, even when melt processed, and also provide excellent moisture barrier properties, making them ideal candidates for the barrier/protective layers of polarizer laminates. COC material suitable to be processed into protective layers in accordance with this invention are disclosed, for example, in US 5,087,677, US 5,324,801, US 5,331,057, US 5,128,446, US  
25 5,225,503, US 5,272,235, US 5,243,005, US 3,557,072, and US 4,178,424.

Such materials may be formed into films suitable for protective layer applications using suitable film-forming processes familiar to those skilled in the art.

The inventive laminates may contain additional layers such as, for example, one or more adhesive layers, other protective and/or support layers, and the like. The present invention further provides a process to make the inventive laminates.

#### Description of the Preferred Embodiments

In one embodiment, the present invention discloses moisture barrier protective layer films comprising cyclic olefin polymer for polarizer laminates. The films generally have a thickness in the range 10 to 1000  $\mu\text{m}$ , preferably in the range 10-500  $\mu\text{m}$ , and typically in the range 10-200  $\mu\text{m}$ . The cyclic olefin polymers useful in preparing the protective layers may be homopolymers or copolymers ("COC") of cyclic olefin monomers. Examples of suitable cyclic olefin monomers are norbornene, tetracyclododecene, bicyclo[2,2,1]hept-2-ene, 1-methylbicyclo[2,2,1]hept-2-ene, hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>8,14</sup>]-4-heptadecene, and the like, and combinations thereof. Many such monomers are well known and are described, for example, in U.S. Patent 5,008,356. In the case of COC copolymers, the comonomer or comonomers are chosen from a variety of suitable olefins, including, for example, acyclic olefins. Many such comonomers are also well known in the literature, including, for example, the above-noted U.S. Patent 5,008,356. Preferred copolymeric compositions as well as a convenient process to prepare them are disclosed in the afore-mentioned U.S. 5,087,677. Such copolymers possess good thermal and optical characteristics, with Tg values typically at least 80°C. The molar percentage of the cyclic olefin

monomer in the COC is generally in the range of 0.1 to 100 %, preferably in the range of 25 to 85 %, and typically in the range of 35 to 75 %. Preferred COCs are the copolymers of norbornene and ethylene in a 50:50 ratio. The Tg of one such 50:50 copolymer, described in the afore-mentioned U.S. 5,087,677 is  
5 135°C. Many grades of the 50:50 norbornene: ethylene copolymer are available from Hoechst Celanese Corporation, Somerville, New Jersey, under the trade name TOPAS™.

The cyclic olefin polymers may be formed into films useful for protective layer applications by a variety of processes well known. These processes  
10 include, but are not limited to, calendaring, extrusion and solution casting, and the like. Such processes may be used to produce COC films exhibiting low birefringence, for example, a birefringence of  $<10^{-4}$  at 633 nm wavelength, and elongations at break of 2-6%. Mechanical properties may also be significantly improved by biaxially orienting the film as described in US Patent Applications,  
15 Serial No. 08/195,077 filed February 14, 1994; 08/195,078 filed February 14, 1994; and 08/195,084 filed February 14, 1994. Birefringence may be minimized during the biaxial orientation by adjustment of process variables such as drawing speed and total stretch ratio in machine and transverse directions. The properties of typical biaxially oriented COC films are shown in Table 1.

**Table 1: PROPERTIES OF BIAXIALY STRETCHED COC FILM USED IN THE  
EXAMPLES**

<b>Polymer:</b>	
COC Polymer:	COC-S-1400 from Hoechst Celanese
5	Corporation
Glass Transition Temperature	135° C
Film Thickness:	30 $\mu$ m
<b>Mechanical Properties:</b>	
10	Modulus: 450 Mpsi
	Tensile Strength: 17.4 Mpsi
	Elongation at break: 80% (machine dir.), 30% (transverse)
	Shrinkage: (15 minutes) 120 C: 0.5%
15	125 C: 1%
	130 C: 20%
<b>Optical Properties:</b>	
	Index of Refraction: 1.53
20	Birefringence: $2 \times 10^{-3}$ (@ $\lambda = 633$ nm)

Furthermore, Table 4 in the EXAMPLES section compares the water permeability of a biaxially oriented COC film useful as protective layer for polarizer laminates with that of a standard cellulose triacetate protective layer.



As Table 4 demonstrates, the water permeability of the COC film is substantially less than that of the CTA film.

Another embodiment of the present invention discloses laminates comprising the above-noted COC-based protective layers and polarizing films.

5 Such laminates possess good mechanical stability, thermal stability and optical clarity. The laminates comprise, in addition to the COC-containing protective layer described above, other layers such as the polarizing layer, adhesive layers, supporting layers, and the like. Some of these categories are described below.

10 Materials suitable for the polarizing layer are known in the art. For example, the polarizing layer may comprise either iodine or a polymer such as, for example, PVA, a polyester, liquid crystalline polymer ("LCP") and the like, along with one or more dichroic absorbers. LCPs are well known in the art, and any suitable LCP may be used in the practice of the invention, provided the  
15 resulting polarizing film has suitable mechanical, thermal and physical properties. The LCP may be a polyester, polyamide, polycarbonate, poly(ester-carbonate), polyaramide, poly(ester-amide), and the like. Preferred LCPs are liquid crystalline polyesters. Several suitable liquid crystalline polyesters are known in the art, such as, for example, the Vectra<sup>®</sup> brand resins supplied by  
20 Hoechst Celanese Corporation, Somerville, New Jersey. Still more preferred LCPs are those disclosed in the pending patent application, Serial No. 08/460,288, filed June 2, 1995. An example from that patent application is the liquid crystalline polyester called COTBPR therein and comprising repeat units from the monomers 4-hydroxybenzoic acid, terephthalic acid, 4,4'-biphenol, 6-  
25 hydroxy-2-naphthoic acid, and resorcinol in the ratio 30:20:10:30:10

respectively. The dichroic absorber may be inorganic such as, for example, iodine, or a suitable organic dye described in the same pending patent application.

The adhesive layer may be made from a thermally curing type adhesive, radiation curing type, pressure sensitive type, x-ray curing type, electron-beam curing type adhesive, and the like. Several such useful adhesives for constructing the laminate are available commercially, such as, for example, acrylic adhesives, acrylic urethane-based adhesives, and the like. Some of them are, for example, Z-FLEX<sup>®</sup> (obtained from Courtaulds Performance Films, Fieldale, Virginia), DEV8154<sup>®</sup> (also called ARclad<sup>®</sup>; obtained from Adhesives Research, Incorporated, Glen Rock, Pennsylvania), UV10LVDC<sup>®</sup> (obtained from Master Bond, Inc., Hackensack, New Jersey), LTX125X<sup>®</sup> and LTX119<sup>®</sup> (obtained from Master Bond, Inc., Teaneck, New Jersey) and 95C21<sup>®</sup> and 95C22<sup>®</sup> (obtained from Sony Chemical Corporation, Tochigi-Prefecture, Japan).

The laminate may contain other optional layers familiar to those skilled in the art. These may include other protective layers, barrier layers, supporting films, substrate materials, and the like. Examples are glasses, ceramics, as well as plastics such as, for example, polyethylene terephthalate (PET), polymethyl methacrylate (PMMA), and triacetyl cellulose (CTA). Other materials such as, for example, polycarbonates, polybenzimidazoles, polybenzimidazolones, polybenzoxazoles, polybenzthiazoles, nylons, polyvinyl chlorides, wholly aromatic polyesters, polyarylates, polyamides, polyaramides, polyimides,

poly(amide-imides), poly(ester-carbonates), poly(ester-amides), and the like may also be used.

Another embodiment of the invention is the process of preparing the laminates. The process generally includes stages such as, for example, curing,  
5 and testing for properties such as mechanical stability, environmental stability, and optical clarity. Prior to the lamination, the surface of the polarizing film may be suitably treated such as, for example, corona plasma, if necessary, to improve its adhesion. Lamination samples comprising the polarizing film, adhesive layer and the protective layer may be assembled, in the order desired.  
10 Thus, for example, the adhesive layer may be applied on one or both sides of the polarizing film, preferably on both, which may then be brought in contact with the protective layer. Or it may be first applied to the protective layer which may then be laminated to the polarizing film. The same adhesive or different adhesives may be used on the two sides although use of the same adhesive is  
15 preferred. The adhesive may be applied by suitable processes which are well known to those skilled in the art, such as, for example, direct application, coating from a solution, extrusion, and the like.

The curing conditions depend on the type of the adhesive - whether it is thermal curing, radiation curing, e-beam curing, and the like. Once the  
20 lamination assembly is prepared, as above for example, the curing conditions such as, for example, temperature, pressure and the like, may be applied to the sample by use of suitable equipment such as, for example, hydraulic press, oven, light (UV, for example) and the like. Vacuum may be used during the curing process to reduce or eliminate any problems with air bubbles. Once the  
25 curing conditions are applied, a certain amount of time is generally allowed for

the adhesive to completely bond the layers. The completion of the lamination may be tested by observing the physical appearance before and after cure. Successful completion of the curing stage depends on the properties of the adhesive, as is well known to those skilled in the art.

5       The testing for mechanical stability involves the testing of the bond strength (peel strength) between the adhesive and the polarizer film after the laminate is cured. Higher peel strength indicates stronger bond between the respective layers, and better mechanical stability. Testing methods for the peel strength are well known in the art, such as, for example, the ASTM D1876  
10       procedure published by the American Society for Testing Materials, Philadelphia, Pennsylvania. The environmental efficiency of the protective layer is tested by measuring the peel strengths before environmental testing of the laminate and thereafter at various time intervals during the environmental testing under conditions that are generally used for testing polarizer films. Such testing  
15       conditions generally involve exposure of the laminate to an elevated temperature and humidity for a specific number of days in order to observe any physical changes in the appearance of the lamination. The longer the lamination is able to withstand the elevated temperature and humidity without significant detrimental change, the greater is its environmental stability, indicating better  
20       protection by the protective layer.

      The laminate may contain other optional layers too. Thus, for example, in one construction of an LCD, the above-described protective layer/adhesive/polarizing film/adhesive/protective layer laminate may be further bonded to a substrate such as glass, plastic, ceramic and the like, by applying  
25       an adhesive to the protective layer and then bringing the substrate in contact

with that layer. The adhesive may be the pressure-sensitive type, for example. The substrate may be bonded to one protective layer only or both. If it is applied to one protective layer only, the laminate will now be, for example, glass/adhesive/protective layer/adhesive/LCP polarizing film/adhesive/protective layer. Additionally, there may also be hard coat layers, anti-reflection coatings, anti-glare layers, birefringent phase-compensation layers and the like. There may also be transparent conducting coatings such as, for example, indium-tin-oxide ("ITO"), which may be coated by processes well known to those skilled in the art. For example, the ITO layer may be directly coated by suitable processes such as vacuum deposition and the like. High Tg COC films are particularly well suited for laminates comprising ITO layers due to the high temperatures required for deposition of such layers. There may also be metal reflectors, transfectors, and the like, as part of the laminate, with or without an adhesive. An example laminate would be metal/polarizing film/adhesive/protective layer/adhesive layer/substrate.

The invention may be illustrated by the following description, wherein an LCP based polarizing film (COTBPR) was used. The adhesive was ARclad DEV8154<sup>®</sup> and the protective layer was a biaxially oriented COC film (COC-S-1400<sup>®</sup> from Hoechst Celanese Corporation). The materials were assembled as described in the EXAMPLES section below, and then cured. The adhesive being a pressure-sensitive adhesive achieved full curing through the use of a hydraulic hot press. The lamination samples cured with the adhesive were then subjected to peel strength testing to determine their bond strength. The cured laminates were then placed into an environmental chamber and exposed to a temperature

of about 90° C and a relative humidity of about 90 percent. These laminates remained in the chamber for a specified number of days in order to observe any physical changes in their appearance and effects on adhesive performance, and tested at several intervals for their peel strength. The testing intervals were one, 5 four, seven, and fourteen days. Results showed excellent adhesion, and no significant deterioration in the peel strength.

For comparison, laminates were similarly prepared using CTA as the protective layer instead of the COC. The peel strength of such laminates significantly decreased in the environmental chamber, thus demonstrating the 10 superior moisture barrier property of COCs for polarizer laminate applications.

The following EXAMPLES are provided to further illustrate the present invention, but the invention is not to be construed as being limited thereto.

#### Examples

15 In the following Examples, two different CTA films were used for comparative purposes. HCCCTA refers to a CTA film manufactured by Hoechst Celanese Corporation, thickness 2.0 mil and available from Catalina Plastics, Las Vegas, Nevada. Eastman CTA refers to KODACEL TA 415™, Item Number K7945, available from Eastman Chemicals, Kingsport, Tennessee., with 20 thickness 3.3 mil.

#### Examples and Comparative Examples:

**Example 1. Illustration of preparing the Laminate:** The LCP used as polarizer in this Example was Vectran A910<sup>®</sup> from Hoechst Celanese Corporation. The protective films were biaxially oriented COC films of 30 micron thickness (see Table 1) from Hoechst Celanese Corporation. The adhesive was

5 ARclad DEV8154<sup>®</sup>. The LCP film was corona treated prior to the application of the adhesive, the adhesive was then applied to the LCP film, and then the protective film was placed on the adhesive, thus preparing the laminate sample. Each laminate sample was then placed into a vacuum bag and then the entire assembly was put into a hot press at 50°C. Table 2 lists the curing conditions

10 and the resulting peel strengths after various intervals of curing time.

**Table 2. Peel Strength Results at Various Curing Pressures**

Lamination sample size: 2"x 4"

Peel Strengths were measured according to ASTM D1876 and are in units of lbs/in.

5	Curing Time (min)	Curing Pressure		
		<u>300 psi</u>	<u>200 psi</u>	<u>100 psi</u>
		<u>COC</u>	<u>COC</u>	<u>COC</u>
	30	4.73	3.49	5.84
10	15	3.27	2.87	3.77
	10	1.56	3.53	1.4
	5	1.82	2.88	1.68
	2.5	5.3	4.53	2.2

15        **Example 2. Preparation and Testing of Laminates containing COC**  
**versus CTA as protective layer.** Similar to the illustration above, laminates were prepared where the polarizing layer was a dyed COTBPR described in the pending patent application, Serial No. 08/460,288, referred to earlier, and the protective layer was either CTA (Eastman as well as HCCCTA) or COC. The  
20 laminates were then subjected to environmental test in order to test the comparative efficiency of the protective layer. The efficiency was determined by measuring the peel strength after regular intervals of time in the environmental chamber. Thus, the peel strength was determined at 0 time in the chamber, and then after intervals of 1, 4, 7 and 14 days in the chamber. Consistently  
25 maintained peel strength without deterioration indicates better adhesion in the



laminate and better protection of the laminate by the protective layer from attack by the humidity conditions. The results are summarized in Table 3:

**Table 3. Peel Strengths Under Environmental Test**

Time (days)	Peel Strength	
	<u>CTA</u>	<u>COC</u>
0	9.24	1.88
1	6.19	2.00
4	0.49	1.05
7	0.18	0.72
14	0.22	1.72

5

The results demonstrate that in the laminate with CTA as the protective layer, the peel strength dropped off very rapidly with progression of time, whereas when COC was used as the protective layer the peel strength stayed nearly  
10 constant, not much different from the starting peel strength. This indicates the superiority of protection by the COC.

Example 3. Water Vapor Permeability Measurements: The water vapor permeability of the biaxially oriented COC film and of the CTA film used in  
15 the above example was compared. The results are shown in Table 4. Permeability was determined by multiplying the measured Water Vapor Transmission Rate (WVTR) by film thickness. A MoCon Permtran-W 3/31 MA module (from (Modern Controls, Minneapolis, Minnesota) was used for measurement of WVTR. The calibration standard S/N 0795AK020, which is

NIST traceable, was used to insure that the unit performed correctly for all tests. For all tests, the calibration standard tested within specifications. A WVTR test temperature of 37.8° C and relative humidity of 100% were used. For samples that tested below 50 grams/meter<sup>2</sup> -day, the samples were unmasked for a test area of 50 cm<sup>2</sup>. For samples above 50 grams/meter<sup>2</sup> -day, the samples were masked to reduce the area to 5 cm<sup>2</sup> so that the detector did not become saturated. The permeability of the 2.0 mil HCCCTA and the Eastman 3.3 mil CTA shows reasonable agreement between the materials made by the two different manufacturers. The comparatively low permeability of COC film versus CTA correlates with the superior performance of COC in maintenance of laminate peel strength after humidity exposure in Example 2. These results confirm the superior protective capability of COC versus CTA in polarizer laminates.

**Table 4. WATER VAPOR PERMEABILITY OF BIAXIALY STRETCHED COC FILM AND CTA FILMS AS DETERMINED BY WATER VAPOR TRANSMISSION RATE**

	<u>HCCCTA</u>	<u>Eastman CTA</u>	<u>COC</u>
<b>Permeability</b>	<b>149</b>	<b>192</b>	<b>5.9</b>
<b>(grams-mil/meter<sup>2</sup></b>			
<b>-day)</b>			
<b>Sample</b>	<b>2.0</b>	<b>3.3</b>	<b>0.8</b>
<b>Thickness (mil)</b>			

CLAIMS

What is claimed is:

1. A laminate comprising: (a) a polarizing film; (b) one or more adhesive layers; and (c) one or more protective layers, wherein said protective layer  
5 comprises a polymer of a cyclic olefin.
2. The laminate as described in claim 1, wherein said protective layer is a cyclic olefin homopolymer.
- 10 3. The laminate as described in claim 1, wherein said protective layer is a cyclic olefin copolymer.
4. The laminate as described in claim 3, wherein said copolymer comprises repeat units of a cyclic olefin monomer and an acyclic olefin.
- 15 5. The laminate as described in claim 4, wherein said cyclic olefin monomer is selected from the group consisting of norbornene, tetracyclododecene, bicyclo[2,2,1]hept-2-ene, 1-methylbicyclo[2,2,1]hept-2-ene, hexacyclo[6,6,1,1<sup>3,6</sup>,1<sup>10,13</sup>,0<sup>2,7</sup>,0<sup>9,14</sup>]-4-heptadecene, and combinations thereof.
- 20 6. The laminate as described in claim 4, wherein said acyclic olefin is selected from the group consisting of ethylene, propylene, 1-butene, and combinations thereof.
7. The laminate as described in claim 5, wherein said cyclic olefin monomer  
25 is norbornene.

8. The laminate as described in claim 6, wherein said acyclic olefin is ethylene.
- 5 9. The laminate as described in claim 4, wherein said copolymer contains 0.1-100 mole percent of said cyclic olefin monomer.
10. The laminate as described in claim 4, wherein said copolymer contains 25-85 mole percent of said cyclic olefin monomer.
- 10 11. The laminate as described in claim 4, wherein said copolymer contains 35-75 mole percent of said cyclic olefin monomer.
12. The laminate as described in claim 4, wherein said copolymer is a  
15 copolymer of norbornene and ethylene.
13. The laminate as described in claim 12, wherein said copolymer is a 50:50 copolymer of norbornene and ethylene.
- 20 14. The laminate as described in claim 1, wherein said polarizing layer comprises polyvinyl alcohol and dichroic absorber.
15. The laminate as described in claim 1, wherein said polarizing layer comprises a liquid crystal polymer and a dichroic absorber.

16. The laminate as described in claim 15, wherein said liquid crystal polymer is selected from the group consisting of a liquid crystalline polyester, polyamide, polycarbonate, poly(ester-carbonate), polyaramide, poly(ester-amide) and combinations thereof.

5

17. The laminate as described in claim 16, wherein said liquid crystal polymer is a liquid crystalline polyester.

18. The laminate as described in claim 17, wherein said liquid crystalline polyester comprises, in its repeat units, residues of 4-hydroxybenzoic acid, terephthalic acid, resorcinol, 4,4'-biphenol and 6-hydroxy-2-naphthoic acid.

19. The laminate of claim 1, wherein said adhesive is selected from the group consisting of thermally curing adhesive, radiation curing adhesive, pressure-sensitive adhesive and mixtures thereof.

15

20. The laminate of claim 1, wherein said adhesive is an acrylic adhesive.

21. A laminate for display applications, comprising a plurality of layers wherein a first layer comprises a blend of a film-forming, thermotropic liquid crystalline polyester and a dichroic absorber, and wherein at least one second layer comprises an adhesive, and further wherein at least one third layer comprises a protective layer comprising a cyclic olefin polymer, and still further wherein said liquid crystalline polyester comprises, in its repeat units, residues of

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4-hydroxybenzoic acid, terephthalic acid, resorcinol, 4,4'-biphenol and 6-hydroxy-2-naphthoic acid.

22. The laminate as described in claim 21, further comprising one or more  
5 layers selected from the group consisting of glass, ceramic, plastic, anti-reflection layer, anti-glare layer, hard coat, reflective layer, transfective layer, and birefringent phase-compensation layer.

23. The laminate as described in claim 21, further comprising a conducting  
10 layer.

24. The laminate as described in claim 23, wherein said conducting layer comprises indium-tin-oxide.

15 25. A process to prepare a laminate comprising the steps of: (a) preparing a polarizing film which film comprises a blend of a liquid crystalline polyester and a dichroic absorber; (b) adhering said polarizing film to one or more protective layers utilizing one or more intermediary adhesive layers, wherein said liquid crystalline polyester comprises, in its repeat units, residues of 4-hydroxybenzoic  
20 acid, terephthalic acid, resorcinol, 4,4'-biphenol and 6-hydroxy-2-naphthoic acid, and further wherein said protective layer is a polymer comprising cyclic olefin moieties in its repeat units.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/08954

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B32B 27/08, B32B 27/32, G02F 1/133  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B32B, G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	File WPI, Derwent accession no. 96-480949, FUJIMORI IND CO LTD: "Optical sheet prodn., useful for electrode base sheet - by casting soln. of compsn. norbornene type resin and crosslinking agent in solvent onto support, drying, and then heat treating"; & JP,A,8244051, 960924 --	1-25
X	EP 0591536 A1 (NIPPON ZEON CO., LTD.), 13 April 1994 (13.04.94), column 3, line 5 - line 10; column 7, line 9 - column 8, line 3, claims 1 and 12, abstract --	1-25

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

- \* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

24 Sept 1997

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

MONIKA BOHLIN

# INTERNATIONAL SEARCH REPORT

International application No.

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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0587890 A1 (NIPPON ZEON CO., LTD.), 23 March 1994 (23.03.94), column 3, line 2 - line 32; column 8, line 13 - line 42, claims 1 and 11, abstract  --	1-25
X	File WPI, Derwent accession no. 93-299328, NIPPON ZEON KK: "Transparent, heat resistant complex sheet for LCD's, car headlight etc. - is prepd. by applying thermoplastic satd. norbornene-type resin sheet onto PVA-type sheet using acryl adhesive then heat treating"; & JP,A,5212828, 930824  --	1-25
X	File WPI, Derwent accession no. 93-058928, HANI T et al: "Durable, heat-resistant polarising film for LCD - has protective layer of thermoplastic satd. norbornane series resin on one or both faces providing low double refraction"; & WO,A1,9302381, 930204  --	1-25
P,A	WO 9638743 A1 (HOECHST CELANESE CORPORATION), 5 December 1996 (05.12.96), claims 1-16, abstract  --	15-18
A	File WPI, Derwent accession no. 92-387864, UENO PHARM CO LTD: "Sheet-form body having polarising property - comprises compsn. contg. thermoplastic polymer e.g. polycarbonate, and liq. crystal polymer e.g. polyesteramide"; & JP,A,4288503, 921013  --	1-25
A	EP 0397263 A1 (N.V. PHILIPS' GLOEILAMPENFABRIEKEN), 14 November 1990 (14.11.90), abstract  -- -----	1-25



SA 53964

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

01/09/97

International application No.

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Patent document cited in search report			Publication date	Patent family member(s)	Publication date
EP 0591536 A1			13/04/94	DE 69213238 D,T	20/02/97
				US 5543948 A	06/08/96
				JP 5002108 A	08/01/93
				WO 9300598 A	07/01/93
EP 0587890 A1			23/03/94	JP 4361230 A	14/12/92
				WO 9222002 A	10/12/92
WO 9638743 A1			05/12/96	NONE	
EP 0397263 A1			14/11/90	DE 69015249 D,T	20/07/95
				JP 3021904 A	30/01/91
				NL 8901167 A	03/12/90
				US 5024850 A	18/06/91